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## Photoelectronic Sensor with Gold Nanoparticle Plasmon Antenna

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## “Photoelectron Sensor with Gold Plasmon Antenna”

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### **Abstract:**

We have proposed a concept of a photo-electronic hybrid device utilizing gold nanoparticles (GNPs), which are supposed to function not only as the Plasmon antenna but also as the sensing part. The photocurrent in the fabricated device, consisting of a transparent Nb-doped TiO<sub>2</sub> channel and Au electrodes, was enhanced more than eight times at a specific wavelength with GNP arrays located between the electrodes, indicating that surface Plasmon resonance was electrically detected with the hybrid device. This result will open new doors for ultra-small biosensor chips integrated with multi-functional solid-state devices.

### **Introduction:**

Surface Plasmon resonance (SPR) and localized surface Plasmon resonance (LSPR) phenomena have gained considerable attention and currently been applied for high-sensitivity biosensors. The frequency and intensity of surface Plasmon absorption bands are sensitive to the type of material and its size, shape, and distribution, as well as to the surrounding media. Thus, the optical response of metal nanoparticles, which are functionalized with acceptors for detecting target biomolecules, informs us of the existence of tiny amount of biomolecules and their reaction kinetics in liquids. For the sensing devices, the scattered or reflected light is collected and/or guided with an objective lens and optical fibers and converted into electrical signals. In spite of the simplicity of the optical detection system, SPR and LSPR-based sensors provide very high sensitivity and have big advantages in the research fields of clinical diagnostics and pharmacology. However, the common optical detection system has definite

limits in terms of miniaturization of equipment size and its integration with functional devices. In addition to the sensing devices, SPR and LSPR phenomena are applicable to optoelectronics and considered as powerful tools that boost performance of various optical circuit devices, such as waveguides and photodetectors. More recently, photodetectors with a distinctive concept have been reported: the Au/nt-Si Schottky photodetector consisting of periodically arranged identical Au nanostructures that play important roles as both Plasmon antennas and Schottky electrodes in contact with the nt-Si layer. The photocurrent in the device strongly depends on the wavelength of incident light, exhibiting the maximum photocurrent at the LSPR absorption wavelength determined by the size and geometry of Au nano-structures. This is because LSPR enhances electron-hole pair generation in Au nanostructures and hot electrons are injected into the semiconductor through the Schottky barrier to amplify photocurrent under reverse bias conditions.

## Experiments, Results and Discussion

### (1) New photoelectric device with gold nano particle Plasmon antenna (To be submitted to Applied Physics Letter)

In our research, aiming at direct electrical detection of plasmonic signals, we extend this concept based on Schottky contact to the photoelectronic hybrid sensing device with a transparent semiconductor channel and Plasmon antenna. We propose a practical and simple concept of the photoelectronic hybrid device utilizing gold nanoparticles (GNPs), which are supposed to function not only as a Plasmon antenna but also as a sensing part to detect surrounding media and biomolecules. The proposed photoelectronic device is schematically shown in Fig. 1. A pair of metal electrodes is formed on a transparent semiconducting layer, and GNP arrays are arranged in the channel region between the electrodes. Fabricating the photoelectronic device involves the following essential challenges: a selective arrangement of high-density GNP arrays in the channel region, material selection, and design for channel and electrodes in order to detect photocurrent enhanced by surface Plasmon. As for GNP arrangement, we had previously developed the selective transport method for GNPs using a ferritin-based encapsulation system. As shown in Fig. 1, this ferritin-based method enables us to form high-density single-layer GNP arrays on  $\text{TiO}_2$  surfaces.

### Fabrication and Evaluation of new opt-electron device

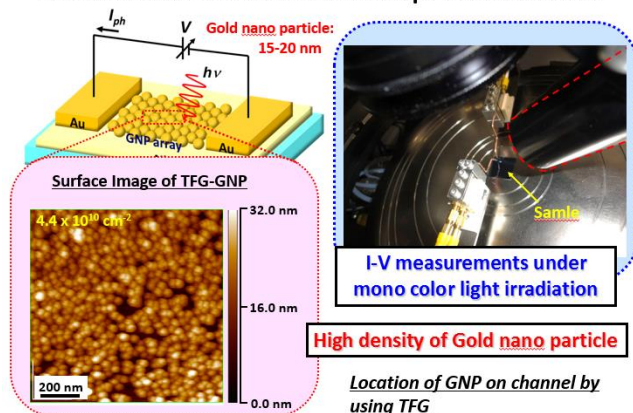


Fig.1 Schematic Image of New Photoelectric Device. A pair of metal electrodes is formed on a transparent semiconducting layer, and GNP arrays are arranged in the channel region between the electrodes

If we assume SPR is excited at the surface of Au electrode, main part of hot carrier composing photocurrent is excited at the surface of Au electrode. Then photo current amplification will be enhanced, if the distance between Au surface and AuNb-TiO<sub>2</sub> interface forming Schottky barriers, is decreased. Therefore, by preparing sample with various Au electrode film thickness ranging from 10 to 50nm, amplification factor at each wavelength were measured as shown in Fig.2. With decreasing Au electrode thickness, photo current amplification factors were increased. When Au electrode is thick, hot carriers are generated by SPR at the surface of Au electrode, however, most of them will be inactivated until they reach Au/Nb-TiO<sub>2</sub> interface. On the other hand, when film thickness is thin, hot carriers by SPR will reach the interface before being inactivated, thus large photo current can be obtained. From these results, enhancement of photocurrent originating from SPR effect was experimentally demonstrated.

### Optimization of device structure

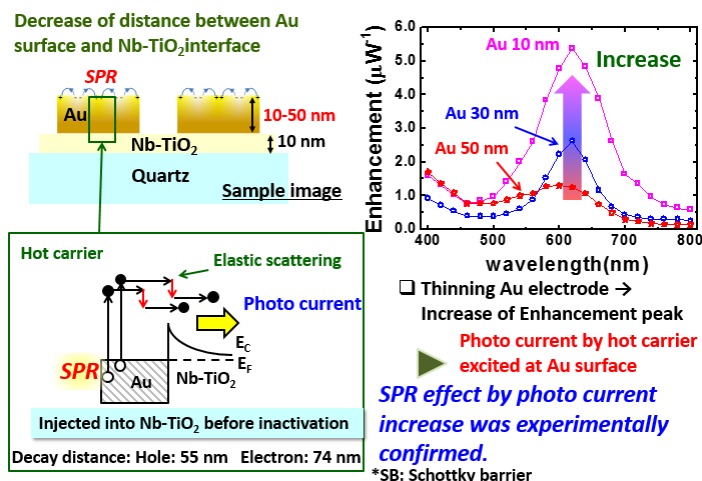
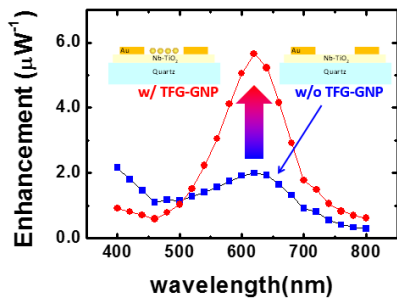


Fig.2 Mechanism of photocurrent generation. With decreasing Au electrode thickness, photo current amplification factors were increased. When film thickness is thin, hot carriers by SPR will reach the interface before being inactivated, thus large photo current can be obtained.

By decreasing Au electrode film thickness to 10nm, improvement of photo current amplification at wavelength of 620 nm was confirmed despite of using GNP. By using this optimized structure, we tried to confirm the improvement of LSPR detection by arraying TFG-GNP on the channel. Photo amplification with various wavelength is shown in Fig.3. As shown in this figure, enhancement of photo current amplification was observed by arraying TFG-GNP similarly with before the optimization. We can conclude that improvement in detection rate of LSPR signal was achieved by using optimized structure.

New opt-electron device with new device structure



Location of TFG-GNP on sample with Au film of 10 nm thickness

□ Peak intensity increased 4 times ( $1.5\mu W^{-1}$  to  $6.0\mu W^{-1}$ ) by structure optimization.

Improvement of LSPR signal detection rate

Fig.3 Photo amplification with various wavelength was measured. Enhancement of photo current amplification was observed by arraying TFG-GNP. Improvement in detection rate of LSPR signal was achieved by using optimized structure.

(2) New photoelectric device with embedded gold nano particle Plasmon antenna (To be submitted to Applied Physics Letter)

We tried to fabricate new photoelectric device using  $TiO_2$  film with embedded gold nano particles as shown in Fig.4. By the irradiation of the light to GNP, light energy is adsorbed by plasmon effect, leading to the generation of hot carriers. These hot carriers are injected over  $Au/TiO_2$  schottky barriers and they are detected as photocurrent. Dependence of photo current and light absorbance is coincided, thus it is concluded that light energy is converted into current.

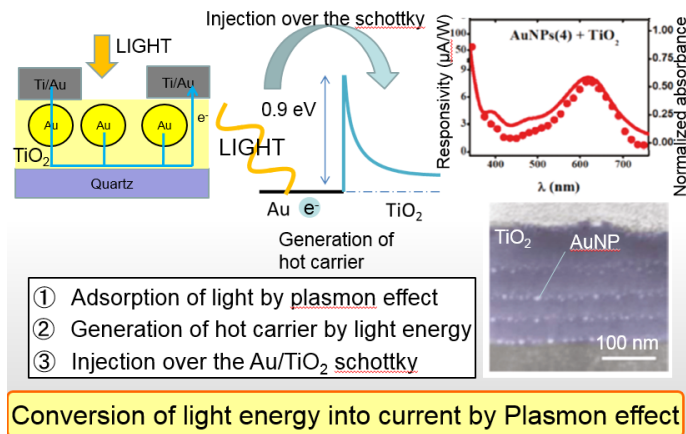


Fig.4. new photoelectric device using  $TiO_2$  film with embedded gold nano particles. By the irradiation of the light to GNP, light energy is adsorbed by plasmon effect, leading to the generation of hot carriers.

Bio nano process is one of the unique technique for controlling nano structure by utilizing protein. We focused on the protein called ferritin. By decorating ferritin with titan precognitive peptide and gold precognitive peptide, we can array GNP on titan substrate. Feature of this method is location control and uniform dispersion (Fig.5).

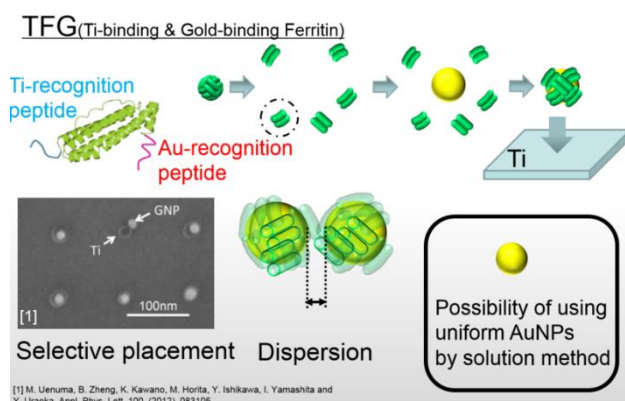


Fig.5. We focused on the protein called ferritin. By decorating ferritin with titan precognitive peptide and gold precognitive peptide, we can array GNP on titan substrate.

In order to improve plasmon antenna property, light absorption property is important. Arraying GNP and shifting the refractive index of surrounding material, change the light absorption property. To detect the change of refractive index, high light absorption and steep spectrum is required. Therefore, high density location on the substrate and uniform dispersion of GNP is strongly required. However, conventional method cannot provide nano dots with uniform size and dispersed array. Thus we employed bio nano process as shown in Fig.6. High density and dispersed GNP are arrayed on the  $\text{TiO}_2$  substrate. In spite of the size, uniformly dispersed nano dot array was obtained.

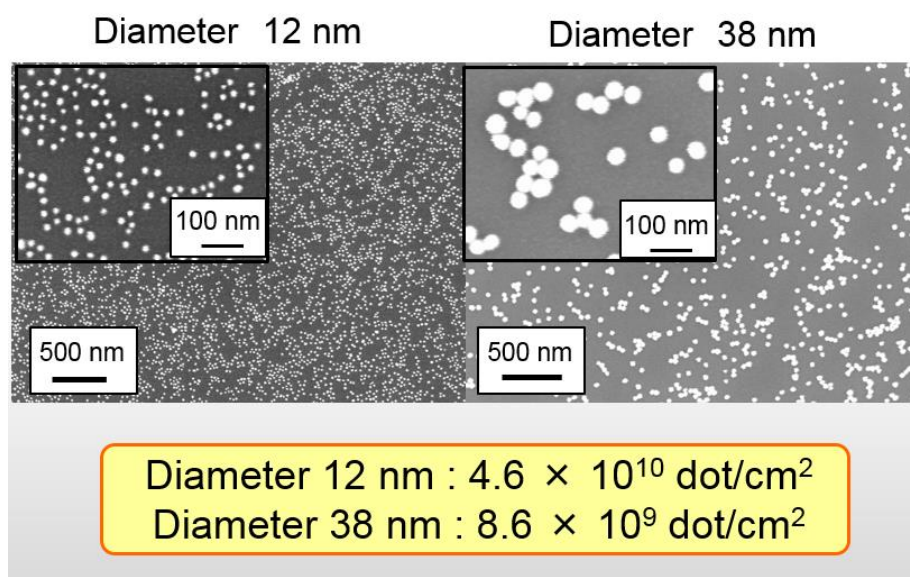


Fig.6. High density and dispersed GNP are arrayed on the  $\text{TiO}_2$  substrate. In spite of the size, uniformly dispersed nano dot array was obtained.



By using GNP array fabricated with bio nano process, we applied them to sensing device and measured optical properties. Fabrication process of bio sensor is as follows: TiO<sub>2</sub> film with 15nm thickness is deposited on glass substrate, GNP is absorbed on the film. After removing outer protein by UV ozone, TiO<sub>2</sub> is deposited again and annealed. As optical properties, reflectance and transmittance is measured. From these measurements, peaks indicating Plasmon effect can be observed at 614 nm. Next we compared the optical properties fabricated with bio nano process and conventional thermal treatment method. We confirmed narrow peak for bio nano process.

Next we measure electrical property of the sample with and without nano dots. We observed photo current at around 300 nm originating from band gap of TiO<sub>2</sub>. And another photo current peak was observed at around 600nm for the sample with and without GNP. We analyzed the peak by peak separation method. We found that this peak can be separated into 5 component and we detected photo current by Plasmon effect as shown in Fig.7. However, unfortunately this component was not remarkable.

We discussed the origin of photo current due to non-Plasmon effect as shown in Fig. 8. Energy levels corresponding to the each component of photocurrent were due to oxygen vacancy in TiO<sub>2</sub> film. Therefore, in order to detect clear Plasmon signal, suppression of oxygen vacancy and high quality TiO<sub>2</sub> film are necessary.

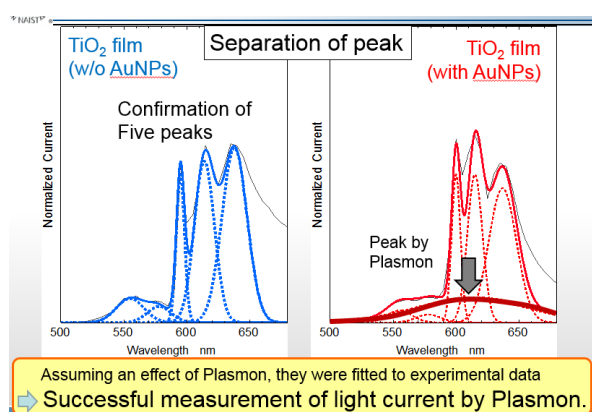


Fig.7. Photo current peak was observed at around 600nm for the sample with and without GNP. We analyzed the peak by peak separation method. We found that this peak can be separated into 5 component and we detected photo current by Plasmon.

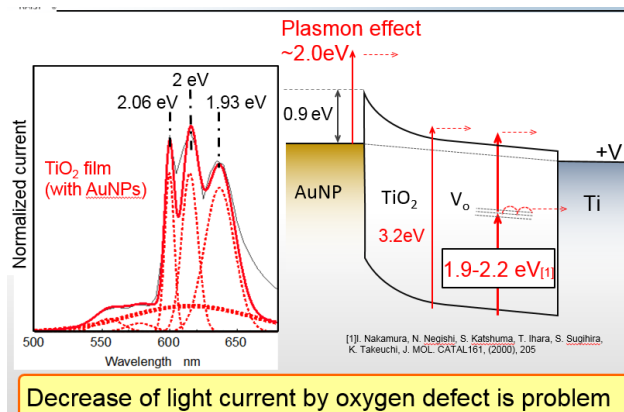


Fig.8. Origin of photo current due to non-Plasmon effect. Energy levels corresponding to the each component of photocurrent were due to oxygen vacancy in TiO<sub>2</sub> film.



### **Young Research (Yasuda) Award**

- 1) Takahiko Ban and Y.Uraoka et al,  
“Ultra-short Channel Floating Gate Memory with a Nanoparticle Array Utilizing Biomaterial”, 2015, Gate Stack Symposium, Shizuoka, Jan., 2015

### **Journal**

- (1) Jonghyeon Jeong, Shinya Kumagai, Ichiro Yamashita, Yukiharu Uraoka and Minoru Sasaki, “Micromechanical IR thermal detector using torsional oscillation: Improvement of resonator profile for high sensitivity”, Japanese Journal of Applied Physics, 54, 04DE07, 2015.
- (2) Takahiko Ban, Mutsunori Uenuma, Shinji Migita, Naofumi Okamoto, Yasuaki Ishikawa, Ichiro Yamashita and Yukiharu Uraoka, “Ultra-short channel junctionless transistor with a one-dimensional nanodot array floating gate”, Applied Physics Letters, 106, 253104 (2015).
- (3) Ippei Inoue, Hirofumi Yamauchi, Naofumi Okamoto, Kenichi Toyoda, Masahiro Horita, Yasuaki Ishikawa, Hisashi Yasueda, Yukiharu Uraoka and Ichiro Yamashita, “Thermo-stable carbon nanotube-TiO<sub>2</sub> nanocomposite as electron highways in dye-sensitized solar cell produced by bio-nano-process”, Nanotechnology 26 (2015) 285601 (8pp).
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- (5) Megumi Fukuta, Bin Zheng, Mutsunori Uenuma, Naofumi Okamoto, Yukiharu Uraoka, Ichiro Yamashita, Heiji Watanabe, “Controlled charged amino acids of Ti-binding peptide for surfactant-free selective adsorption”, Colloids and Surfaces B: Biointerfaces Volume 118, 1 June 2014, Pages 25-30.
- (6) Tatsuya Hashimoto, Yurie Fukunishi, Bin Zheng, Yukiharu Uraoka, Takuji Hosoi, Takayoshi Shimura, and Heiji Watanabe, “Electrical detection of surface plasmon resonance phenomena by a photoelectronic device integrated with gold nanoparticle plasmon antenna”, Appl. Phys. Lett. **102**, 083702 (2013)

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- (1) Yana Mulyana, Mutsunori Uenuma, Naofumi Okamoto, Yasuaki Ishikawa, Ichiro Yamashita and Yukiharu Uraoka, "Detection of Ferritin on Graphene-based Field-Effect Transistor for Bio-sensing Application", BIT's 1st Annual World Congress and EXPO of Smart Materials-2015, Young Investigator Forum, BEXCO, Busan, Republic of Korea, March 2015.
- (2) Hiroki Kamitake, Mutsunori Uenuma, Naofumi Okamoto, Yasuaki Ishikawa, Ichiro Yamashita, Yukiharu Uraoka, "Fabrication of 3D nanodot array using Dps-DNA self-assembly", Pacificchem 2015, MTLs 809, Hawaii Convention Center, Honolulu, Hawaii, Dec. 16, 2015.
- (3) Takahiko Ban, Mutsunori Uenuma, Shinji Migita, Naofumi Okamoto, Yasuaki Ishikawa, Ichiro Yamashita, Yukiharu Uraoka "Ultra-short Channel Floating Gate Memory with a Nanoparticle Array Utilizing Biomaterial", Pacificchem 2015, MTLs 831, Hawaii Convention Center, Honolulu, Hawaii, Dec. 17, 2015.
- (4) T. Nonaka, Y. Uraoka, N. Taguchi, S. Yamamoto, "Interdigital Electrodes Technologies for Distributed Inorganic EL Displays", PHp1-7L, The International Display Workshops Volume 21, 558, Niigata, Dec.3-5, 2014.
- (5) S. Ishikawa, T. Miyasako, H. Katsui, K. Tanaka, K. Hamada, C. Kulchaisit, M. Fujii, Y. Ishikawa, Y. Uraoka, "Reliability of Amorphous InGaZnO Thin Film Transistors with Low Water-Absorbed Passivation Layer", AMD3-2, The International Display Workshops Volume 21, 558, Niigata, Dec.3-5, 2014.
- (6) D. Hishitani, M. Horita, Y. Ishikawa, Y. Watanabe, H. Ikenoue, Y. Uraoka, "Formation of Solution-Derived SiO<sub>2</sub> Thin Films by CO<sub>2</sub> Laser Annealing for Polycrystalline Silicon Thin Film Transistors", AMD8-3L, The International Display Workshops Volume 21, 558, Niigata, Dec.3-5, 2014.
- (7) T. Tomikawa, J.-H. Jeong, S. Kumagai, I. Yamashita, Y. Uraoka, M. Sasaki, "DESIGNING POSITIONS OF GRAIN BOUNDARIES IN Si THIN-FILM FOR LOWENERGY- LOSS OPTICAL MEMS/NEMS DEVICES", 2014 International Conference on Optical MEMS and Nanophotonics, 17-21 August 2014, Glasgow, Scotland
- (8) J.-H. Jeong, S. Kumagai, I. Yamashita, Y. Uraoka, M. Sasaki, "VIBRATIONAL IR MEMS SENSOR: APPLICATION OF TORSION-BARS TENSIONENHANCED BY BIO-NANO CRYSTALLIZATION FOR HIGHLY SENSITIVE DETECTION", 2014 International Conference on Optical MEMS and Nanophotonics, 17-21 August 2014, Glasgow, Scotland
- (9) J.H. Jeong, S. Kumagai, I. Yamashita, Y. Uraoka and M. Sasaki, "A Micro-Machined IR Thermal Detector Using Torsional Oscillation:Improvement of Resonator Profile

for High Sensitivity”, SSDM 2014, Tsukuba International Congress Center, 8-11, Sep. 2014, Tsukuba, Japan.

- (10) M. Uenuma, I. Yamashita and Y. Uraoka, “Find Filament in ReRAM using Thermal Analysis”, SSDM 2014, Tsukuba International Congress Center, 8-11, Sep. 2014, Tsukuba, Japan.

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